

NATIONAL REFERENCE LIBRARY  
OF SCIENCE AND TECHNOLOGY

26 NOV 1968

11 CA

No. 797,917

45

ISSUED Oct. 29, 1968



52

CLASS 401-51  
C.R. CL.

10

# CANADIAN PATENT

11

BRIDGED POLYMERS

George B. Feild, New Castle, Delaware, U.S.A.

Granted to Hercules Incorporated, Wilmington, Delaware, U.S.A.

12

APPLICATION No. 923,969

13

FILED

Feb. 23, 1965

14

PRIORITY DATE Mar. 13, 1964 (351,818) U.S.A.

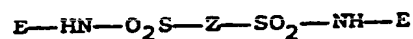
No. OF CLAIMS 7 - No drawing

This invention relates to bridged polyethylene and bridged polyethylene--elastomer alloys of improved properties. More specifically, this invention relates to polyethylene and polyethylene--elastomer alloys bridged with sulfonamide groups.

Recent advances in the art of polymerization have enabled the preparation of ethylene polymers including alloys with other polymers valuable for a variety of uses. These ethylene polymers in the raw state are deficient in certain properties such as hardness, stiffness, environmental stress  
10 cracking, gas permeability, solvent permeability, melt strength at low shear, etc. It is known in the art to cross-link these polymers, as for example with peroxides, in order to change their properties. Such cross-linked polymers are compression moldable and extremely useful in applications where resistance to solvents and elevated temperatures are important. However, they are insoluble after cross-linking and can no longer be considered thermoplastics, capable of being extruded, injection molded, or processed by other methods requiring melt flow.

It has now been discovered that ethylene polymers  
20 bridged with sulfonamide groups can be prepared which are completely soluble in the usual polyethylene solvents but have greater resistance to environmental stress cracking, greater hardness, stiffness, higher melt strength at low shear, and lower permeability to gases and liquids. These bridged polymers extrude smoothly with reduced sag due to their higher melt strength and can be thermoformed into a variety of useful articles.

Accordingly, this invention relates to a solid, thermoplastic polyethylene containing sulfonamide bridges  
30 with the structure



where E is polyethylene and Z is an organic radical free of hindering groups, said sulfonamide bridges comprising from about 0.001% to about 0.075% by weight, based on the total weight of the bridged polymer. The expression "free of hindering groups" means that Z does not contain a group which will interfere with the bridging reaction. For example, Z may contain one or more free sulfonazide groups, which are not hindering groups. The bridged ethylene polymer of this invention is completely soluble in perchlorethylene at a temperature of 110°C. and can be ex-  
10 truded smoothly and thermoformed at temperatures only slightly higher than the unbridged polymer. The unique bridged ethylene polymers of this invention begin to crystallize at a higher temperature and crystallization is more rapid than with unbridged polyethylene. The resulting crystallized bridged polymer exhibits a higher density and a marked improvement in environmental stress cracking.

Any linear polyethylene including alloys of linear polyethylene with from about 1% to about 25% of an elastomeric hydrocarbon polymer, containing not more than about 5% by weight  
20 of unsaturation, and most preferably completely saturated, can be used in the preparation of the bridged polyethylene of this invention. Exemplary elastomeric hydrocarbon polymers which can be alloyed with the polyethylene are polyisobutylene, butyl rubber, ethylene--propylene copolymer, ethylene--propylene--dicyclopentadiene terpolymer, etc.

Any polysulfonazide, i.e., any compound having the general formula  $R(SO_2N_3)_x$  where R is an organic radical inert to bridging reactions and x is from about 2 to about 8 can be used. Most preferably, x will average about 2 and R will be  
30 selected from the group of organic radicals consisting of alkylene, halogenated alkylene, arylene, aralkylene and alkarylene radicals. Exemplary polysulfonazides are the alkyl

797917

sulfonazides such as 1,5-pentane bis(sulfonazide), 1,8-octane bis(sulfonazide), 1,10-decane bis(sulfonazide), 1,10-octadecane bis(sulfonazide), etc., the aryl bis(sulfonazides) such as 1,3-benzene bis(sulfonazide), 4,4'-diphenyl methane bis(sulfonazide), 4,4'-diphenyl bis(sulfonazide), 1-octyl-2,4,6-benzene tris(sulfonazide), 4,4'-diphenyl ether bis(sulfonazide), 1,6-bis(4'-sulfonazidophenyl) hexane, 2,7-naphthalene bis(sulfonazide), etc., and mixed sulfonazides of chlorinated aliphatic hydrocarbons containing an average of  
10 from about 1 to 8 chlorine atoms and from about 2 to 5 sulfonazide groups per molecule.

The bridging reaction is carried out by heating the ethylene polymer in the presence of the polysulfonazide to a temperature at which the sulfonazide decomposes, i.e., generally in the range of from about 100°C. to about 250°C. The amount of polysulfonazide used will be sufficient to yield a bridged polymer containing from about 0.001% to about 0.075% by weight of sulfonamide bridges.

The polysulfonazide bridging agent can be incorporated  
20 in the ethylene polymer by a number of methods. For example, it can be uniformly blended by simply milling on a conventional rubber mill, by extrusion, or dissolved in a solution or dispersion containing the polymer. By any of these methods, the bridging agent is distributed throughout the polymer and uniform bridging is effected when the mixture is heated.

The bridged ethylene polymers of this invention can contain additives as, for example, extenders, fillers, pigments, stabilizers, plasticizers, flame retardants, etc. However, there are many cases in which a bridged ethylene polymer containing an additive is not required or desired and excellent  
30 products are obtained which have nothing added to them except the bridging agent.

797917

The following examples are presented to illustrate the unique bridged ethylene polymers of this invention. All parts and percentages are by weight unless otherwise indicated.

Examples 1-3

In each example, 100 parts of a finely divided linear polyethylene, having a density of 0.945 and melt index of 0.3, was wet with acetone containing the desired amount of polysulfonazide bridging agent and 0.1 part of 4,4'-thiobis (3-methyl,6-tert-butylphenol) stabilizer. A mixed sulfonazide of a chlorinated aliphatic hydrocarbon containing on an average 11 carbon atoms, 2 chlorine atoms and 2 sulfonazide groups per molecule was used as the bridging agent. The acetone was evaporated with stirring and the resulting powder dried under vacuum at a temperature of 60°C. Each powdered mixture was fed into a 1-1/4 inch extruder with a 20:1 length: diameter ratio, a screw speed of 35 r.p.m. and a temperature gradient over the length of the barrel of 360°F. to 430°F. The extrudate immersed as strands from a 0.125 inch die into a water bath. The resulting extrudates were examined for surface smoothness, weighed to determine extrusion rates and chopped into pellets. Pellets of each composition were compression molded at a temperature of 347°F. for 8 minutes under a pressure of 500 p.s.i. into 4" x 4" x 0.075" sheets and tested for resistance to environmental stress cracking when bent 180° while immersed in an aqueous solution of nonylphenol ethyleneoxide adduct (nonionic detergent). Results of the tests during extrusion and resistance to environmental stress cracking are shown in Table I.

797917

Table I

Ex. No.	Sulfon- azide parts/ 100	Extru- sion Rate g./min.	Extru- date Surface	Extru- date Density	Resistance to Environmental Stress Cracking in Hours		
					20% Fail	50% Fail	90% Fail
1	0	97	Smooth	0.9390	80	112	142
2	0.03	98	"	0.9395	116	152	207
3	0.05	101	"	0.9404	164	208	268

From the above it can be seen that the bridging of  
 10 polyethylene with polysulfonazides effects a marked improve-  
 ment in environmental stress cracking without sacrifice in  
 extrudate surface quality or rate of extrusion.

Example 4

The polyethylene described in Examples 1-3 was blended  
 with 1,3-benzene bis(sulfonazide) and 4,4'-thiobis(3-methyl,  
 6-tert-butylphenol) stabilizer exactly as described in Examples  
 1-3. A portion of the powdered blend was extruded into strands  
 as described in Examples 1-3. The resulting strands were  
 evaluated for surface roughness and extrusion rate and then  
 20 chopped into pellets for melt index determinations. Another  
 portion of the blend was extruded downward through a cross-  
 head die and tested for sag by the following procedure. After  
 12 inches of polymer strand had been extruded, it was grasped  
 at the die with forceps and allowed to cool while hanging in  
 a vertical position. The increased length of the cooled strand  
 compared with the original 12-inch length was the measure of  
 sag. This measure is an indication of melt strength under low  
 shear stress. A control sample of the polyethylene was blended  
 and tested in the same way except the disulfonazide was omitted.  
 30 Results of the tests are tabulated below.

797917

	<u>4</u>	<u>Control</u>
1,3 benzene bis(sulfonazide)	0.03	0
Melt Index ( $I_2$ at 190°C.)	0.23	0.31
Extrudate Surface	Smooth	Smooth
Extrusion Rate, gms./min.	99	98
Per cent Sag	1.5	14.7

#### Examples 5-7

Samples of the pellets described in Examples 1-3 were extruded as parisons using a 1-1/2 inch extruder at a temperature of 410°F. and a screw speed of 45 r.p.m. and the resulting parisons blown into standard Boston round type, 4-oz. bottle molds. Less parison sag was observed in the compositions containing the polysulfonazide, resulting in more uniform wall thickness from the top to the bottom of the bottles. Sections of the side walls of the bottles were tested for density and flexural stiffness. The results are tabulated in Table II.

Table II

20	<u>Example No.</u>	<u>Sulfonazide Parts/100</u>	<u>Bottle Wall Density</u>	<u>Flexural Stiffness p.s.i.</u>
	5	0	0.9459	70,000
	6	0.03	0.9475	77,000
	7	0.05	0.9478	77,500

#### Examples 8-10

Molding pellets containing various amounts of polysulfonazide were prepared as described in Examples 1-3. The mixed sulfonazide described in Examples 1-3 was used as the bridging agent. Pellets from each molding composition were tested for melt index and then injection molded into a spiral mold at a temperature of 390°F. using a pressure of

797917

800 p.s.i. The concentration of polysulfonazide, melt index and length of the injection molded spiral for each composition are shown in Table III.

Table III

<u>Ex. No.</u>	<u>Sulfonazide Parts/100</u>	<u>Melt Index (I<sub>2</sub> at 190°C.)</u>	<u>Spiral Length (mm.)</u>
8	0	0.27	108
9	0.025	0.21	112
10	0.050	0.12	108

10 It can be seen from the above that in spite of the considerable reduction in melt index caused by the bridging reaction, no significant difference was shown in melt flow within the spiral mold under identical high shear stress conditions.

Examples 11 and 12

20 In each example, 100 parts of a finely divided linear polyethylene having a density of 0.945 and a molecular weight of approximately 150,000 was wet with acetone containing the desired amount of polysulfonazide and 0.1 part of 4,4'-thiobis(3-methyl,6-tertiary butylphenol) stabilizer. The mixed sulfonazide described in Examples 1-3 was used as a bridging agent. The acetone was evaporated with stirring and the resulting powder dried under vacuum at a temperature of 60°C. Each powdered mixture was milled on a 2-roll mill for 12 minutes at a temperature of 340°F. and then chopped into pellets. Each set of pellets was injection molded into tensile specimens at a cylinder temperature of 450°F. and 800 p.s.i. pressure. The melt indexes of the pellets and properties of the injection molded specimens are tabulated below.



797917

	<u>Example Number</u>	
	<u>11</u>	<u>12</u>
Sulfonazide parts/100	0	0.05
Melt Index ( $I_2$ at 190°C.)	0.15	0.08
Density of molded specimens	0.9455	0.9461
Tensile Strength (p.s.i.)	6060	6800
Tensile Modulus (p.s.i.)	134,000	154,000

From the above it can be seen that the polymer bridged with polysulfonazido processes equally well as the unbridged polymer and is higher in density, strength, and stiffness.

#### Examples 13 and 14

In each example, a linear polyethylene, having an annealed density of 0.957, a molecular weight of 147,000 and no detectable unsaturation, was blended with a polysulfonazide, extruded and chopped into pellets as described in Examples 1-3. The mixed sulfonazide described in Examples 1-3 was used as the bridging agent. A portion of the pellets were compression molded into 0.075 inch sheets at 350°F. for 10 minutes under 800 p.s.i. pressure and tested for flexural stiffness. Another portion of the pellets were injection molded into a spiral mold as described in Examples 8-10. The results of these tests are tabulated below.

	<u>Example Number</u>	
	<u>13</u>	<u>14</u>
Sulfonazide parts/100	0	0.075
Extrudate Surface	Smooth	Smooth
Extrusion Rate (gms./min.)	105	104
Melt Index ( $I_2$ at 190°C.)	0.75	0.22
30 Density of Molded Product	0.9470	0.9510
Flexural Stiffness of Molded Product	73,500	86,500
Spiral Length (mm.)	90	88

797917

From the above it can be seen that the bridging of saturated linear polyethylene results in improved density and stiffness without any sacrifice in flow properties during extrusion.

Examples 15-24

To show the criticality of polysulfonazide bridging agents, samples of linear polyethylene having a density of 0.945, and a melt index of 0.30, were blended with various amounts of either 1,10-decane disulfonazide or a commercial  
10 peroxide cross-linking agent. Each sample was blended, extruded and chopped into pellets as described in Examples 1-3. A portion of each extrudate was fed into a water cooling bath, evaluated for surface roughness, chopped into pellets and then evaluated for melt index. Another portion was extruded without cooling and tested for sag as described in Example 4. The results of these tests are shown in Table IV.

Table IV

Ex. No.	Additive	Additive parts/100	Extrudate Appearance	Melt Index	Per cent sag
20 15	-	0	Smooth	0.33	14.6
16	1,10-decane disulfonazide	0.010	"	0.30	6.1
17	"	0.020	"	0.27	2.0
18	"	0.030	"	0.25	0
19	"	0.050	"	0.21	-2.0
20	2,5-dimethyl-2,5-di(tert-butylperoxy) hexyne-3	0.001	Slightly rough	0.24	5.0
21	"	0.005	"	0.20	2.0
30 22	"	0.010	Rough	0.17	0
23	"	0.020	"	0.12	-1.4
24	"	0.030	Very rough	0.10	-3.0

797917

From the above can be seen the surprising difference between the effects of the two additives on the rheological properties of polyethylene. At equal concentrations, the peroxide makes a greater reduction in melt index and sag but causes extrudate roughness, even in amounts as small as 0.01 parts/100.

Examples 25 and 26

Examples 11 and 12 were repeated except that in each case 10 parts of polyisobutylene (having a molecular weight of 90,000) per 100 parts of polyethylene were added during the 2-roll mill compounding. Results of the tests on these bridged alloys are tabulated below:

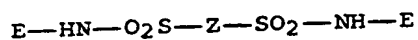
	<u>Example Number</u>	
	<u>25</u>	<u>26</u>
Sulfonazide, parts/100	0	0.05
Density of molded specimens	0.9475	0.9498
Tensile Strength (p.s.i.)	5450	5900
Tensile Modulus (p.s.i.)	115,000	133,000

\* \* \* \* \*

The bridged polyethylene polymers of this invention are useful in a number of applications such as in blow molding, paper coating, vacuum forming and other applications where less heat distortion is required. Their higher densities and stiffness allows their use in bottles, films and packaging applications. Their improved stress crack resistance is of particular importance in detergent bottles, wire and cable insulation and piping.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A solid thermoplastic polyethylene soluble in perchlorethylene at a temperature of 110°C. containing sulfonamide bridges with the structure



where E is polyethylene and Z is an organic radical free of hindering groups, said sulfonamide bridges comprising from about 0.001% to about 0.075% by weight of the bridged polymer.

2. The composition of Claim 1 wherein the polyethylene is linear polyethylene.

3. The composition of Claim 1 wherein the polyethylene is alloyed with polyisobutylene.

4. The process of preparing shaped polymer articles which are soluble in perchlorethylene at a temperature of 110°C. which comprises heating a mixture of an ethylene polymer and from about 0.001% to about 0.075% by weight of polyethylene of a sulfonazide having the general formula  $R(SO_2N_3)_x$  wherein R is an organic radical inert to bridging reactions and x is an integer from about 2 to about 8.

5. The process of Claim 4 wherein the mixture is extruded.

6. The process of Claim 4 wherein the mixture is injection molded.

7. The process of Claim 4 wherein the mixture is extruded and then thermoformed.

